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TRANSITION METALS IN SUPERHEAT MELTS. Petr JAKES (Faculty of Sciences, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic) and Michael-Patrick WOLFBAUER (Bemidji State University, Bemidji MN)

A series of experiments with silicate melts doped with transition element oxides was carried out at atmospheric pressures of inert gas at temperatures exceeding liquidus. As predicted from the shape of fO_2 buffer curves in T- fO_2 diagrams the reducing conditions for a particular oxide-metal pair can be achieved through the T increase if the released oxygen is continuously removed. Experimental studies suggest that transition metals such as Cr or V behave as siderophile elements at temperatures exceeding liquidus temperatures if the system is not buffered by the presence of other oxide of more siderophile element. For example the presence of FeO prevents the reduction of Cr_2O_3 . The sequence of decreasing siderophilicity of transition elements at superheat conditions (Mo, Ni, Fe, Cr) matches the decreasing degree of depletion of siderophile elements in mantle rocks as compared to chondrites.

The partition of elements between the metal and silicate phases is of importance in the study of Earth's and other planetary cores and the behavior of iron and moderately siderophile elements, i.e., elements that may occur in natural minerals in both oxidic and metallic form provide constraints on the mantle-core relationship. We have been interested in the behavior of those siderophile elements that are moderately depleted in the upper mantle of the Earth since the observations of natural objects, i.e., tektites, meteoritic ablation spherules, lunar glasses (e.g., Jakes et al., 1992) indicate that very high temperatures of silicate melts may involve structural changes (due to breaking bonds between oxygen and metal) of the melts and may ultimately lead to siderophile behavior of transition elements (Mo, Cr, V) as well as Si.

In order to assess the behavior of elements in the metal/silicate system in relation to increasing temperature (superheat melts) we have carried out a series of experiments in which we studied the behavior of transition elements, especially their partition between the metal and silicate phases at superheat conditions.

Three significantly different compositions were studied:

(1) JAP represents a composition with extremely high contents of refractory elements and it is close in composition to eutectic of $CaMgSi_2O_6$ - $CaAl_2SiO_6$ - $CaTiAl_2O_6$. This composition is similar to refractory "igneous" inclusions in carbonaceous meteorites. We have synthesized two derivative compositions by doping JAP with Cr_2O_3 and MoO_3 .

(2) LBI represents a composition of potential lunar "oxygen" ore composed of 50% Apollo 11 basalt simulant and 50% ilmenite. Whereas the JAP composition has zero content Fe, this (LBI) is extremely Fe rich.

(3) Indochinite composition represents high Si melts (terrestrial-type superheated melt) with relatively low Fe contents.

Indochinite composition was prepared from natural indochinite; JAP and LBI compositions were mixed from chemicals.

Experiments were run in a Deltech vertical furnace in a nitrogen atmosphere. The samples were run in platinum or alumina crucibles at 1300°, 1425°, and 1550°C each for a period of three hours. Carbon sleeve was positioned around the experimental charges to act as a buffer and to prevent oxidation of the system. We believe that both oxygen brought to the system with the nitrogen gas and oxygen released from melts due to high-temperature-induced reduction were reacted with carbon sleeve. No physical contact between the carbon and capsule containing the

melt was allowed. At the end of the run, the compositions in platinum were quenched in liquid nitrogen, the aluminum crucibles were cooled on switching the furnace. The experimental charges were examined optically and using the electron microprobe. In an analytical procedures platinum was used as a representative of metallic phase and concentrations of metals were measured at the boundary of silicate and metal phases. None of the experiments could be considered to have reached equilibrium.

Generally, the reaction of metal oxide with the metallic phase (represented) by the Pt capsule is dependent on temperature and hence fO_2 . There is a positive correlation between temperature and the amount of particular metallic oxide entering a metallic state. As temperature increased more FeO to Fe took place, apparently releasing oxygen as a byproduct of superheating (in high-silica highly viscous melts, for example, more bubbles are observed). In alumina crucibles a few metallic grains of Fe were precipitated from melt in LBI composition run for period of three hours (LBI composition was mixed from trivalent iron oxide reactants). In a superheat melt less siderophile element enters a metallic state only in the absence of an oxide of more siderophile element (e.g., the presence of FeO prevents reduction of Cr_2O_3). Interesting results were obtained in an experiments where superheated (LBI) melt was seeded with metallic seeds containing the (87%) and Cr (13%). After quenching, all precipitated metal at the bottom of the alumina capsule was Fe and had less than 0.1% Cr, whereas quenched silicates were Cr, Al, and Ti rich. In experiments with no Fe present (JAP), Cr and Mo were noted to enter the metallic (platinum) phase, though in the experiments with no Cr and Mo, minute amounts of Ti entered the Pt capsule.

The formation of metallic species from silicate melts is definitely temperature controlled and metal formation (i.e., high-temperature-induced reduction) strictly buffered by the presence or absence of other transitional-siderophile metals or their oxides.

There are two major implications of these experiments: (1) superheating (temperature-induced reduction) itself could be used for the production of oxygen in the lunar environment through the thermal decomposition of Fe silicates and oxides and (2) it is very difficult to envisage the formation of a siderophile depletion pattern characteristic of the upper mantle of the Earth by simply mixing two components, one reduced the other oxidized. The sequence of T- or fO_2 -controlled events or mixing of components with different degrees of reduction must be sought.